

Smart Selection Principles of Electrode Materials for Lithium-Ion Batteries in Electric Vehicles

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Abstract: It is heatedly discussed that reducing carbon dioxide emissions is exceptionally essential for today's environment. It is believed that replacing petrol vehicles with electric vehicles (EVs) is a decent solution to lower emissions. Therefore, the booming of EVs is desired. Because the batteries are the core for the performance enhancement of EVs, an increasing number of research has been developed for their judicious preparation. With the advancement of critical components, especially innovative electrode materials, lithium-ion batteries (LIBs) have received widespread attention as the most popular secondary cells due to their lightweight and high theoretical specific capacity. This review presents the development history and practical application of advanced electrode materials used in LIBs, including anode and cathode materials. Further, I will also overview the distinguishable characteristics of the LIBs mentioned above to summarize the potential application and highlight the looking-forward perspectives in this rapidly growing field.

1. Introduction

Secondary batteries are considered important, and they can be utilized in electric vehicles and energy storage. There are many researchers conducted to look for decent batteries with lightweight, high theoretical specific capacity, driving ranges, and so on to meet the requirements for electric vehicles. Moreover, that is why the importance of LIBs is gradually highlighted. Lithium is the lightest element with the lowest reduction potential among all metals. Lithium metal is an ideal cathode material because of its theoretical specific capacity of 3861 mAh g^{-1} , extensive exchange current density, and small polarization. Lithium as a negative electrode or lithium ion-containing compounds as a positive electrode of the battery are collectively considered lithium batteries. The most commonly used LIBs are secondary lithium batteries which can be charged and discharged repeatedly. Lithium secondary batteries include secondary lithium batteries and LIBs. Secondary lithium batteries typically show lower energy density and the formation of lithium dendrites in the process of repeated charge and discharge cycles. Thus, they are gradually replaced by LIBs.

However, there are still some challenges to address. When the LIBs are used in portable electronics, the batteries, with LiCoO_2 as the cathode electrode and graphite carbon as the anode material, can meet most of the products' needs. With the market of EVs booming, if LIBs will be used in EVs, they have to have the qualities of lower cost, higher thermal stability, more driving ranges, and so on. Because electrode materials largely determine whether batteries can be used in EVs, researchers pay more attention to optimizing the batteries by designing new methods for synthesizing the electronics and looking for new electrode materials or materials with new structures.

In this review article, the promising materials of LIBs in the EV market are introduced. The working principles of LIBs are firstly explained, which can show the motion of lithium ions and the function of anode materials and cathode materials. Then, the paper will mainly exhibit the electrode materials with three kinds respectively and give detailed information on their history, advantages and disadvantages, the solutions for the present difficulties, and some typical research findings. Because the electrode materials used in LIBs for EVs are the focus of this article, the characteristics of various electrode materials mainly used today will be summarized and analyzed in the next part. In addition,

some practical cases will be given. Furthermore, I will also analyze the performances of different EVs with their LIBs.

2. Working Principle of LIBs

In 1981, Goodenough et al. used materials with layered structure as the cathode material, overturning the conventional thinking that lithium ions need to come from anode materials. The interconversion of electric energy and chemical energy can be achieved through the intercalation and deintercalation of lithium ions between the anodes and the cathodes, thus completing the battery's repeated charging and discharging process.

In the charging process in LIBs which take graphite carbon as the anode material and LiCoO_2 as the cathode material, lithium ions will be leached out from the cathode material. After the electrolyte and diaphragm embedded graphite, the positive electron donors at this time, for the high potential of rich lithium, discharging lithium ions from graphite again and embedding LiCoO_2 . During the discharge process, lithium ions are released from graphite and embedded into LiCoO_2 . At the same time, electrons are obtained from the positive electrode, and electrons and lithium ions migrate between the anode and the cathode so that redox reactions occur between the electrodes to complete the discharge process.

At present, various researches have been carried out to improve the working efficiency of LIBs. Electrode materials, as one of the cores of LIBs, have become the main object of optimization of battery components because of their high development cost and decisive role in the charge and discharge performance of LIBs. In the following parts, carbon-based materials, silicon nanoparticles, transition metal oxides, and LMO are selected as representative examples for in-depth comprehending of designing highly efficient electrode materials in LIBs.

3. Electrode materials

3.1 Anode materials

3.1.1 Carbon-based materials

Carbon is the electrode material studied widely among the various anode materials because of its low energy consumption, environmental friendliness, thermal stability, and solid electronic conductivity. However, as a kind of carbon material, graphite has a specific capacity of 372 mAh g^{-1} , which is not enough to meet the needs of electric vehicles. In addition, due to the low working potential of a graphite material, the LIBs are easy to produce branch crystallization. To solve these problems, many people use carbon nanowires, carbon nanotubes (CNTs), and other carbon-based nanomaterials instead of graphite. These porous carbon nanomaterials can shorten the transport distance of electrons and ions and provide a large specific surface area, which can help improve the lithium storage performance.

In 2009, Landi et al. alleviated the first cycle charge loss and paper crystallinity for free-standing CNT electrodes [1]. They thought that using open-ended structures and enriched chiral fractions of semiconducting or metallic chiralities could improve capacity and electrical transport in CNT-based LIBs. In 2018, Li et al. used a green method to prepare carbon nanofiber electrode material. They synthesized boron-doped porous carbon nanofiber electrode material by bacterial cellulose and three-dimensional porous structure. Furthermore, after the electrochemical performance test, it was found that the specific capacity of LIBs still had 1300 mAh g^{-1} after 120 cycles at 100 mA g^{-1} current density and had 390 mAh g^{-1} after 800 cycles at 500 mA g^{-1} . It shows that the materials have great potential as anode material for electric vehicle batteries and are expected to be applied on a large scale.

3.1.2 Silicon nanoparticles

Nowadays, silicon nanoparticles gradually replace the commonly used graphite and become a promising anode material with a high theoretical gravimetric capacity of 4200 mAh g^{-1} [2]. However,

during the lithiation process, there is an enormous strain because of the electrode volume expansion of approximately 400%, resulting in the void spaces between the particles and lead to the battery's poor contact. To solve this kind of problem, the preparation of well-designed nanostructures is a good choice. Furthermore, optimizing the Si electrode by integrating Si with various carbon materials is also heatedly discussed nowadays.

With the thermal reduction, Wen et al. prepared Si nanotubes converted by silica nanotubes [3]. This kind of Si showed a much smaller change with less than 20% capacity loss from 1929 mAh g⁻¹ to 1545 mAh g⁻¹ in the first two discharge cycles compared with commercial silicon meshes, which proved its improved long-term cycling performance. As another solution, introducing carbon can reduce the volume expansion and simultaneously increase the electrical contact with surrounding conducting materials. Thus, Liu et al. fabricated the carbon-silicon complex with a yolk-shell structure [4], which can have a high capacity of 2800 mAh g⁻¹ at C/10, the long cycle life of 1000 cycles with 74% capacity retention, and high Coulombic efficiency of 99.84%.

3.1.3 Transition metal oxides (TMOs (TM = Co, Ni, Fe, Cu))

These materials are gaining increasing attention because of their abundance and much higher theoretical storage capacities when it comes to transition metal oxides.

With alumina membranes as the templates, Chen et al. designed the synthesis of α -Fe₂O₃ nanotubes [5], which showed a high specific surface area displayed excellent electrochemical activity, including a very high discharge capacity of 1415 mAh g⁻¹ at 100 mA g⁻¹. However, many challenges remain to be addressed, such as low mass-loading electrodes, poor electrical conductivity, and limited cycle numbers.

To this end, Wang et al. used solid-electrolyte interphase (SEI) film and rGO to optimize the structure of the materials [6], which alleviated the fading of the capacity. Then they tried to use porous graphitic carbon to encapsulate the materials, and they finally found that the electrode they made had a very stable capacity until 1000 cycles.

3.2 Cathode materials

3.2.1 LiCoO₂

As the original cathode material for LIBs, LiCoO₂ has brought significant changes to people's lives by developing mobile phones, tablet computers, and other electronic products. LiCoO₂ is a material with high lithium content, strong recycling ability, and high electrochemical stability. Therefore, even 30 years after its birth, LiCoO₂ is still widely used in the market. Nevertheless, because LiCoO₂ will release oxygen at high temperatures and the oxygen produced can have an exothermic reaction with the organic matter in the battery, this material also has high toxicity. At the same time, although it can be used in portable electronic products, the low power density of LiCoO₂ makes it difficult for large-scale battery preparation and transportation.

To apply LiCoO₂ to EVs, reducing the particle size is an effective way to improve the power density. Kawamura et al. mixed lithium acetate with cobalt acetate in a particular proportion and then calcined the mixture into powder at 600 °C for 6 h [7]. Finally, the powder was washed with a large amount of water to remove impurities and dried to obtain spherical LiCoO₂ nanoparticles with a diameter of about 25 particles. The discharge capacity of the material can be increased to 100 mAh g⁻¹. Doping new elements is also an effective way to improve cathode materials. In recent years, a new cathode material, LiNi_xCo_yMn_zO₂ (NCM), has been studied extensively. Introducing nickel elements has higher energy density, and manganese elements can make it have good cyclic stability. In addition, the reduced cobalt content reduces production costs and toxicity [8]. In 2018, Ku et al. adopted the hot solvent method to manufacture rich lithium manganese cathode material (Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂) [9]. After electrochemical testing, it was found that the material had a high initial discharge capacity of 276 mAh g⁻¹ at 0.1 C, and the initial coulomb efficiency increased by 87.6%. After 200 cycles at 1 C, the reversible capacity was 231 mAh g⁻¹ and the capacity retention rate was 95.8%, showing excellent electrochemical performance.

3.2.2 LiMn₂O₄ (LMO)

As the voltage increases, a phase transition will happen in LMO's structure from cubic to tetragonal crystal structure, known as Jahn-Teller distortion, which also damages the structural integrity of the electrode during the charge/discharge cycle and leads to rapid capacity decay [10]. Even at 4 V, capacity decay occurs at elevated temperatures. There are two ways to solve this problem, one is to reduce the particle size, and the other is to dope the material with other ions.

The nanoscale electrode material can increase the contact area between electrode and electrolyte and promote charge transfer and diffusion during lithium insertion/de-embedding, thus improving the resistance of electrode material to structural changes and thus optimizing the stability of the battery. At present, many manufacturers will focus on using nano-sized LiMn₂O₄ as cathode materials to prepare LIBs. Initially, nanoscale LiMn₂O₄ is prepared by wet chemical methods (including the sol-gel, combustion, precipitation, spray pyrolysis, and hydrothermal synthesis). Then in most cases, chelating agents are added to assist the synthesis in preventing complicated aggregation during subsequent calcination.

In 2012, Tang et al. used metal salts containing the starch as the raw material and prepared nanochain LMO by the sol-gel method [11]. After the electrochemical test, they found that the battery they made had great reversible capacity. For example, at 20 °C, the reversible capacity was 58 mAh g⁻¹. In addition, its reversible capacity was 70 mAh g⁻¹ at 1 C, and the results showed that the nanochain lithium manganate cathode had an excellent performance rate.

However, the reduction of particles alone cannot completely solve the capacity decay problem. The electrolytic process may separate individual nanoparticles or aggregates from the electrode, leading to irreversible loss of capacity and electrode integrity. At the same time, as a semiconductor, LiMn₂O₄ conductivity is relatively low. To solve these problems, researchers often add conductive and stable materials to electrode materials. In 2012, Lee et al. reported a synthetic three-dimensional porous LiMn₂O₄/carbon nanocomposite [10]. When the nanocrystals obtained by low-temperature water treatment were mixed with sucrose and quenched at 600 °C, the electrode material obtained had a high-rate performance. It maintained a capacity of 83.1% at 50 °C. Accordingly, finding an efficient and easy way to coat a highly conductive carbon layer remains a challenge.

3.2.3 LiFePO₄ (LFP)

As one of the most promising cathode materials for the next generation of LIBs, LFP can be used for large-scale applications such as electric vehicles and hybrid electric vehicles. Compared with LMO, LFP, whose theoretical rate capacity is up to 170 mAh g⁻¹, has better chemical and thermal stability, low cost, and is non-toxic. However, their poor electrical conductivity and low diffusion constant of lithium ions hinder its sizeable current charge and discharge. Toward this, using a carbon coating on the particle surface or conductive polymers, amorphous materials to reduce grain size, heat treatment, and other methods are usually adopted.

The use of carbon coating is the focus of research. In 2010, Damen et al. prepared a solid-state polymer lithium metal battery with an LFP/C composite cathode and a poly (ethylene oxide) PEO-based solid polymer electrolyte and found that the battery made in their way surpassed the goals stated by USABC-DOE, leading to the conclusion that this kind of battery could be used in EVs [12]. Then in 2013, Ma et al. synthesized the olivine-type niobium doping Li_{1-x}Nb_xFePO₄/C (x=0, 0.005, 0.010, 0.015, 0.025) via a two-step ball milling solid-state reaction [13]. According to the electrochemical test, the composite exhibited the best electrochemical performance with a discharge capacity of 139.3 mAh g⁻¹ at 1 C rate. However, many current methods remain in the stage of complicated operation and high raw material cost.

Recently, transforming waste batteries to synthesize better electrode materials has also become a direction for preparing LFP. In 2019, Wei et al. regenerated the LFP cathode material via the hydrothermal method and then recovered the graphene oxide from the spent graphite anode by the Hummers method [14]. The materials made this way presented smaller and more uniform spherical particles and exhibited reversible capacities of 162.6 mAh g⁻¹ and excellent rate capacity. Whatever

electrochemical properties or economic efficiencies were considered, the composites they made were better than those regenerated by solid-phase roasting in today's EV industrialization.

3.3 Overall comparison and analysis

Since Sony's commercialization in 1991, rechargeable LIBs, which have high energy density and long cycle life become the most popular power source for most portable electronics and even the most promising candidate for EVs. Due to low energy consumption and environmental friendliness, carbon-based materials are the most common anode for LIBs. However, their low theoretical capacity of 372 mAh g^{-1} is the main challenge because a power source with high energy density and high-power density is needed in EVs [6]. Silicon nanoparticles, with a high capacity of 4200 mAh g^{-1} , can meet EVs' needs. However, there is still a significant concern in the volume expansion of silicon nanoparticles, which can lead to strain during the lithiation. Even worse, the expansion can expose the silicon to the electrolyte, resulting in the formation of the solid-electrolyte interphase SEI [15]. Moreover, the surface of silicon will repeatedly be renewed, and it will consume the lithium-ion and form excessive SEI, which can lead to the deterioration of the batteries' circulation.

Transition metal oxides with high specific capacities are considered the most promising anode alternatives. However, optimizations need to be developed because of the poor electrical conductivity and the significant changes in the lithium ions' insertion and extraction process.

LiCoO₂, the first material used in LIBs for portable electronics, is gradually replaced due to their toxicity by other cathode materials, such as LMO and LFP. Better operational performance happens in the operation of the LIBs with LFP than those with LMO. In addition, fewer batteries are needed over the EV service life. Through doping and nanoparticle formation, those materials can be improved in electrochemical performance.

4. Practical application of lithium-ion batteries in electric vehicles

Almost all EVs rely on LIBs now, and it is reported that LIBs have the highest energy, long life, and acceptable abuse tolerance. In 2009, Motohira et al. tested the run of the electric bus with the LIBs, which are made from LiAl_{0.05}Mn_{1.95}O₄ used as cathode and graphite and hard carbon used as anode [16]. They found that the LIBs made in this research can satisfy electric buses' needs, such as the energy density, power density, and the number of cycles.

In 2010, as the beginning of the EVs, the first generations of vehicles had a 100-mi range or below. The vehicles from Nissan Leaf, for example, had a 70-mi range with LMO as their cathode materials. However, EVs currently have a range of more than 100-mi, such as Tesla with over 200-mi and the Chevrolet bolt, published in 2017, with the range of 240-mi [17]. Table 1 below provides several types of LIBs for EVs.

Table 1. Types of LIBs for different EVs.

Product model	Battery type	Battery weight (kg)	Nominal driving distance (km)	Top speed (km/h)	Charge time (h)	Release year
Nissan leaf	LMO (With LiNiO ₂)	294	117-200	150	0.5-20	2010
BMW i3	NMC	230	130-160	150	0.5-9	2013
Tesla Model S	NCA	535-556	370-426	193-214	0.5-1.25	2012
BYD e6	LFP	500	330	140	2-10	2010
citron C-zero	LTO	165	127	130	0.25-6	2010

5. Conclusions

In this review article, I discuss the development and the traits of various electrode materials. As the materials in the LIBs of the first generation, LiCoO_2 and graphite were gradually replaced by other electrode materials, which can offer higher specific capacities, lower cost, and so on. Electrode materials in LIBs for EVs are constantly updated. The silicon-based materials are constantly optimized because of their volume expansion. Considering the most potential anode materials, TMOs also need to be improved because of their poor electrical conductivity and the significant changes during their working process. When it comes to the cathode materials, LFP and LMO are both promising materials. Furthermore, there are many ways to improve them, such as different doping elements or reducing the size of the materials. However, the problem following that is the cost increases and the performance changes, which still need to be reconsidered.

Vehicle electrification has now gained tremendous momentum worldwide, and the large number of existent EVs and future launched ones also reflect this. Long-range EVs, high-end plug-in hybrid electric vehicles and micro hybrids appear to be the vehicle platforms currently receiving the most attention. LIBs, which primarily use LMO cathodes and graphite anodes, meet the main requirements of the batteries used in these vehicles.

Currently, several battery systems are under development that may have higher energy density and lower cost. However, based on the current state of battery system research and development, it is clear that the next generation of automotive batteries will still be based on advanced LIBs. Furthermore, with the increasing number of researches on the LIBs in EVs, the performance of the EVs has been optimized. Nevertheless, there are still many challenges for researchers to solve for better chemical performance, higher BMS efficiency, and lower cost.

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